Pressure-induced anomalous isotopic fractionation of Li in magmatic hydrothermal systems

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Lithium has been demonstrated to undergo significant fractionations in geological environments, both elementally and isotopically. Such fractionations have been shown to occur due to various processes, with both chemical and kinetic effects contributing to the observed partitioning. Isotopic fractionation in particular, has been used to constrain processes of fluid release in the slab and mantle wedge through to the degassing of magmas and the subsequent condensation of hydrothermal fluids and fumarolic gases.

In this study, lithium isotope fractionation between synthetic granite and aqueous Cl bearing fluids was investigated experimentally. Experiments were conducted at 800°C and between 1.0-2.8 kbar, with the salinity of the fluid varying between 0, 0.1, 1 & 10 wt% NaCl. A strong systematic fractionation of ^{7}Li into the fluid of 1 - 10‰ was observed, with the strongest fractionations occurring at higher Cl concentrations. However, the most marked effect is that caused by pressure, with the fractionation doubling between 2.0 and 2.8 kbar.

Ab initio calculations of isotopic fractionation between $Li(H_2O)_4^+$ and $LiCl_n(H_2O)_{4-n}^{1-n}$ predict values of Δ^7Li ($Li(H_2O)_4^+$-$LiCl_2(H_2O)_2^-$) near +5 ‰ at 1000ºC but in ideal gas at zero pressure. Accordingly, we would expect the fluid to increasingly favour the light isotope due to Cl complexation. However, we find that the fluid strongly favours the heavy isotope with increasing Cl. We attribute this to a very strong pressure effect on isotope fractionation between $Li(H_2O)_4^+$ and $LiCl_n(H_2O)_{4-n}^{1-n}$. For a 0.1*m* Cl solution Δ^7Li (fluid-glass) increases by 4‰ with a 0.8 kbar pressure increase.

In summary, Li is light enough to still undergo substantial isotopic fractionation even at magmatic hydrothermal temperatures. However, the effect of pressure is comparable, and opposite, to that of temperature and complexation by Cl. The interpretation of Li isotopes measured in natural systems must account for these competing effects. On the other hand, the isotopic composition of Li offers potential as a geobarometer at elevated T.

Petrografic and geochemical characteristic of metagreywackes (Central Portugal): implication of Zr content

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Introduction

Petrography and geochemistry (major, trace and rare earth elements) of two greywackes samples from the Upper Proterozoic to Lower Cambrian "Complexo Xisto-Grauváquico – CXG" (Central Portugal) have been investigated as support of subsequent mineralogical study of zircons. The two samples: Alv 51 and Alv 55 are close one to another (ca 20m), being the last near a fault zone.

Results

The petrographic and geochemical studies have shown significant differences: (i) Alv 51 is a metagreywacke in chlorite zone conditions, with a clastic texture and an anisotropic mica-quartz matrix. Anisotropy is marked by a spaced anastomosing foliation, with microlithons controlled by the size of quartz and plagioclase porphyroclasts. Detrital zircons are presents as accessory mineral with euhedral oscillatory zoning crystals (60-120 μm). (ii) Alv 55, near the fault zone, presents heterogranular granoblastic texture, with quartz, chlorite, calcite, muscovite, sphene and rutile, resulting from local hydrothermal metamorfism. Detrital zircons are not identified, but chlorite shows pleochroic haloes associated with very small zircons (1-2 μm) and abundant rutile needles.

The major elements composition of the samples is quite different: Alv 51 is richer in SiO_2 and K_2O while Alv55 present higher content in all the others major elements, especially in MgO, TiO_2, P_2O_5, but also in CaO and Na_2O. The trace elements content is also very different. Alv 55 shows an enrichment of LREE, Ba, Sr, Ni, Cr, and especially Hf, Th and U. This sample has higher Zr content (Alv 55 Zr= 376ppm; Alv 51 Zr = 275ppm). The UCC [1] normalized spider plot highlights these differences.

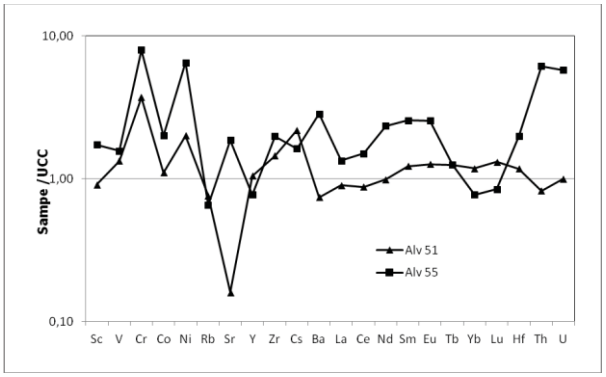

Figure 1: UCC [1] normalized spider plot.

The high content of Cr, TiO_2 LREE, Hf, Th and U and low contents of HREE in Alv55 may suggest that the Zr is partly associated with the rutile (anatase) and not only with the zircon. The incorporation of Zr in rutile, by substitution of Ti is favored by increasing temperature and is used as geothermometer [2].

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[1] Taylor,McLennan (1985). The C Crust…Blackwell, 312p

[2] Zack *et al* (2004) *Contrib Mineral Petrol* ,**148:** *471-488*.